Oxidative and non-oxidative degradation of a TDI-based polyurethane foam: volatile product and condensed phase characterisation by FTIR and solid state ^{13}C NMR spectroscopy

D. Allan, J. Daly, J. J. Liggat*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK

*CORRESPONDING AUTHOR Ph: +44 (0)1415484351 Email: j.j.liggat@strath.ac.uk;

ABSTRACT

The oxidative and non-oxidative degradation behaviour of a flexible polyurethane foam, synthesised from toluene diisocyanate and a polyether polyol, is reported. Both toluene diisocyanate and diaminotoluene were identified as major products under non-oxidative conditions, which indicates that the urethane linkages are degrading by two competing degradation mechanisms. Degradation of the urethane linkage by a depolymerisation reaction to yield toluene diisocyanate and polyol is proposed to occur initially. In addition, the atmospheric pressure conditions favour the degradation of the urethane linkages *via* a six-membered ring transition state reaction to form diaminotoluene, carbon dioxide and alkene terminated polyol chains. Solid-state ^{13}C NMR spectroscopy and elemental analysis of the residues indicates that at temperatures above 300°C ring fusion of the aromatic components within the foam occurs, and this leads to a nitrogen-containing carbonaceous char which has a complex aromatic structure. It is proposed that under the confined conditions of the degradation the aromatic nitrogen-containing species, such as toluene diisocyanate and diaminotoluene, undergo secondary reactions and ring fusion to yield a complex char structure.

Under oxidative conditions, degradation, including ring fusion, occurs at a lower temperature than under non-oxidative conditions. Neither toluene diisocyanate nor diaminotoluene were observed as major degradation products. The polyol is observed to undergo thermo-oxidative degradation at much lower temperatures than purely thermal degradation. As a consequence, the depolymerisation reaction *via the* six-membered ring transition state is limited in extent and diaminotoluene is not evolved. The absence of toluene diisocyanate is proposed to be a result of this species undergoing oxidative degradation reactions which lead to it being incorporated into the char.

KEYWORDS Polyurethane foam; TDI; solid state NMR; condensed phase; thermal degradation; oxidation.

1. INTRODUCTION

Polyurethanes are one of the most versatile classes of polymers which find vast use in today's society yet their use as furnishing and insulation materials has been implicated as a contributory factor in tragedies such as the 1979 Manchester Woolworths fire and the 2016 London Grenfell Tower fire. The major drawback of these materials is their flammability and the toxic nature of the gases which are evolved upon combustion. The behaviour of a polymer in a fire is closely associated with its thermal and thermos-oxidative degradation behaviour but polyurethanes are complicated materials which can contain a variety of functional groups and the degradation behaviour of polyurethanes is, therefore, complex.

Given their importance, it is no surprise that there is a considerable literature on the thermal degradation chemistry of polyurethanes [see for example 1-13], although studies on foam materials are more limited in number, with many studies focussing on elastomers or model compounds.

The degradation of a complex material like polyurethane can be expected to begin at the thermally weakest linkage within the polymer chain. Polyurethanes can contain up to six types of major linkages which undergo thermal degradation at different temperatures: urethane, urea, biuret, allophonate, ether and ester. Biuret and allophonate groups are the thermally weakest of the major linkages, undergoing thermal degradation in the temperature range 110°C to 170°C [1, 2]. The next most thermally stable group is the urethane link, which begins to cleave around 170°C, with the process becoming more significant at 200°C [2]. The urea group is the next most thermally stable, followed by the ester and ether groups within the polyol moiety of the polyurethane. Rigid foams often contain a high proportion of isocyanurate linkages and these are reported to be more stable than any of the nitrogen-containing linkages and possibly more so than the ether and ester groups [1, 2].

It is generally accepted that the purely thermal degradation of the urethane linkages within polyurethane (the primary degradation step) occurs between 200°C and 250°C by one or more of three mechanisms: (i) a simple depolymerisation to regenerate isocyanate and hydroxyl groups, (ii) a six-membered cyclic transition state producing amine and alkene chain ends and CO_2, (iii) a four-membered transition state liberating CO_2 without chain scission. It has been reported by many authors that the depolymerisation reaction (i) is the predominant degradation reaction for the urethane linkage [2, 3, 5-7].

Following the primary degradation step, the polyol or polyol-based material generated will then undergo degradation reactions to produce a variety of degradation products containing hydroxyl, carboxyl, carbonyl and ether groups [8-13].

In our previous paper [14], we reported on the thermal degradation of a toluene diisocyanate foam under high vacuum conditions, with a focus on the characterisation of volatile degradation products. Our evidence indicated that the initial degradation step corresponds to degradation of the urethane linkages by two competing mechanisms. The first mechanism, proposed to be the predominant mechanism, involves the simple depolymerisation of the urethane bond to yield TDI and polyol. A second, competing, mechanism involving the six-membered transition state yield diaminotoluene, carbon dioxide and alkene-terminated polyol chains. The amines were then proposed to react in the vapour phase with the regenerated TDI to yield polyurea. Secondary degradation processes could be attributed primarily to degradation of the polyol which was regenerated in the first degradation step. Isothermal studies revealed that this occurs as low as 250°C under vacuum but does not become significant until temperatures greater than 300°C. Degradation of the polyol is proposed to occur by random radical chain scission to yield propene, formaldehyde, acetaldehyde, C_3H_6O isomers and high molar mass polyol chain fragments of various structures.

The stability of polyurethanes under an oxidative environment is of great importance to polymer scientists as under most applications the material will be exposed to air for prolonged periods of time. In particular, the thermo-oxidative behaviour of polyurethane foams is of significance when considering the fire behaviour of these materials, as the polymer will be exposed to both high temperatures and oxygen during the course of a fire.

Thermal degradation in the presence of oxygen usually occurs at a lower temperature and a faster rate than in the absence of oxygen [15]. The oxidation of polymers is an auto-catalytic process, *i.e*. the rate is slow initially but gradually accelerates as the reaction proceeds. The oxidation of polymers proceeds *via* a free radical chain mechanism and, like other radical mechanisms, consists of three steps (initiation, propagation and termination). The overall mechanism for thermo-oxidative degradation follows the general mechanism outlined in Scheme 1 [15-17].

Initiation: $RH \rightarrow R^{\bullet} + H^{\bullet}$

Propagation: $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$

Termination: $2R^{\bullet} \rightarrow R - R$

$R^{\bullet} + ROO^{\bullet} \rightarrow ROOR$

$2ROO^{\bullet} \rightarrow ROOR + O_2$

Scheme 1: General mechanism for polymer oxidation.

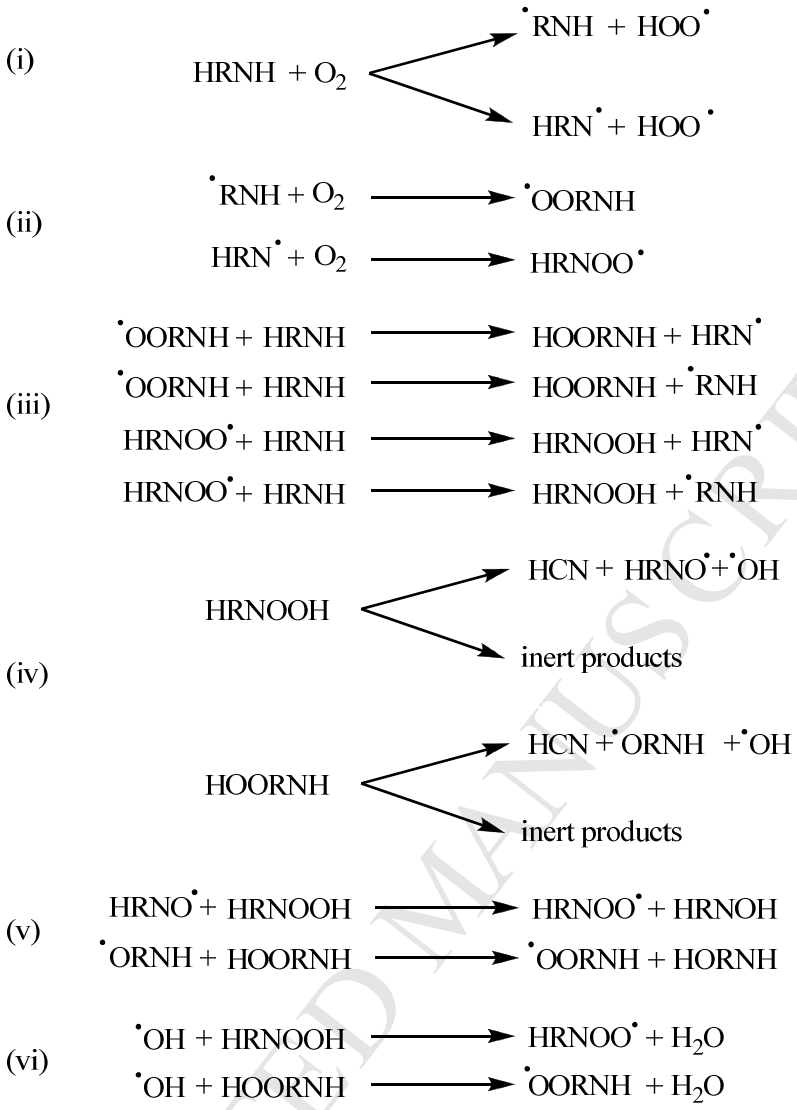
Initially free radicals $(R^{\bullet})$ are produced which subsequently react with molecular oxygen to form peroxy radicals $(ROO^{\bullet})$. The peroxy radicals abstract hydrogen from the polyurethane chain resulting in the formation of hydroperoxides $(ROOH)$ which then undergo thermal decomposition to yield more radicals which can further react with the polyurethane chain. This sequence of events leads to discolouration of the material and a loss in the physical properties [18].

The soft segments in polyurethane are reported to be more susceptible to oxidative degradation than the hard segments [18], making the products of thermo-oxidative degradation strongly dependant on the nature of the polyol employed. In some cases [19, 20] it has even been reported that the presence of oxygen does not influence the primary degradation step of the polyurethane, *i.e.* depolymerisation of the urethane linkages to yield diisocyanate and polyol. Benbow and Cullis [19] observed that the first stage of degradation of TDI-based polyurethane foams under air, attributed to loss of isocyanate fragments, occurred at the same temperature as under an inert atmosphere. These results were later corroborated by Bilbao *et al.* [20]. Furthermore, polyurethanes based on polyether polyols have been shown to be more susceptible to oxidative degradation than their polyester counterparts. [18, 21, 22]

Wlodarczak [23] studied the thermo-oxidative degradation of a polyurethane foam from 200°C to 700°C by means of degradation-GC-MS. The major volatile degradation products

which were identified included CO, CO_2, methanol, C1-C4 aliphatic hydrocarbons, acetonitrile, acrylonitrile and HCN. Isothermal experiments conducted at intervals of 100°C revealed that the concentrations of HCN, hydrocarbons and CO_2 increased with increasing temperature, whilst the methanol, acetonitrile and acrylonitrile concentrations peaked at 500°C.

Jellinek and Dunkle [24] studied the thermo-oxidative degradation of a number of polyurethanes synthesised from a variety of polyols and isocyanates. They proposed that for all polyurethanes a thermo-oxidative mechanism can be postulated based on the original mechanism proposed by Boland and Gee [16] involving the formation of hydroperoxides which then degrade *via* radical chain reactions leading to deterioration of the polyurethane. The thermo-oxidative mechanism proposed by Jellinek and Dunkle is presented in Scheme 2 where HRNH represents a typical polyurethane.



Scheme 2: Mechanism of thermo-oxidative degradation of a polyurethane as proposed by Jellinek and Dunkle [24]

In this paper, we present data on the degradation of a TDI-based PU foam, with a focus on the characterisation of the condensed phase. Degradation studies were conducted to further probe the degradation behaviour of the polyurethane under non-oxidative environments. Similar to the TVA experiments [14], a wealth of information can be gained from degradation studies including mass loss data and characterisation of cold-ring fractions and residues. These degradation studies, however, differ from the TVA experiments in that the degradation is not conducted under vacuum, which could be deemed more representative of a fire situation. Furthermore, different gases can be employed during the degradation allowing the degradation to be studied under a variety of environments. Finally, these degradation studies allow the use of significantly larger sample masses, which leads to the generation of

sufficient quantities of condensed phase products to facilitate characterisation of this material. Char formation is one of the most important condensed-phase mechanisms for modifying the combustion process of a polymer and by studying the structure of the condensed phase formed during the degradation information can be gained with regards to the condensed-phase behaviour of the polyurethane. The degradation of the foam was studied under three different environments: nitrogen, air and 3% oxygen in nitrogen, the latter representing the vitiated conditions of a typical fire.

2. MATERIALS AND METHODS

2.1 Materials

Flexible polyurethane foam was prepared in the University of Strathclyde following a patented flexible foam formulation. [25] The isocyanate employed was TDI (with an isocyanate index of 108) and the polyol was Alcupol F-5611 (a trifunctional polyether polyol of molar mass 3000 g mol^{-1} and hydroxyl index 56 mg KOH g^{-1}). Typically, the isocyanate was incorporated at a level of 46 parts per hundred polyol (pph). Water (3 pph) was employed as the blowing agent and the catalysts employed were dimethylethanolamine (DMEA, 0.3 pph), triethylenediamine (Dabco 33LV, 0.3 pph) and stannous octoate (Kosmos 29, 0.8 pph). A silicone-based surfactant (L620LV, 1 pph) was also employed. It should be noted that the levels of surfactant and catalyst present are sufficiently low to assume that these do not participate in or affect the degradation reactions which occur.

2.2 Degradation

Degraded samples were prepared using a degradation rig which had been designed and constructed for this purpose. The equipment comprised of a block heater in which borosilicate sample tubes were positioned. Each tube was fitted with a specially designed head which allowed a gas stream to be passed over the sample and the volatile degradation products to be vented from the tubes. Four tubes could be connected simultaneously.

Sample holders were made by wrapping a square section of aluminium foil around the end of a test tube to create a cylinder shape. This was done to allow easy removal of the sample from the tubes after the degradation, allowing post-degradation analysis to be carried out. Cylinders of foam with masses in the range 200-300 mg were then cut and placed inside the

foil sample holders. Samples of this size were used in order to generate enough residue to allow characterisation of the residue by solid-state ^{13}C NMR.

Each foam was degraded at four different temperatures under nitrogen, air or 3% oxygen in nitrogen. The degradation temperatures employed were the same as those used for the isothermal TVA experiments reported in [14], *i.e.* 250, 300, 350 and 400°C. At each degradation temperature four samples of the same foam were degraded in order to ensure reproducibility of the results and to ensure that an adequate level of residue was generated to allow solid-state ^{13}C NMR analysis. Each degradation run followed the same general experimental procedure as outlined below:

1. The aluminium sample holders and foam samples were weighed and the combined mass recorded before being inserted into the sample tubes.
2. The tubes were placed into the block heater and the tube heads connected to the degradation rig by means of screw-top connectors and rubber tubing.
3. The gas of choice was then fed into the degradation tube at a rate of 40 ml min^{-1}, allowing a gas flow of 40 ml min^{-1} to reach each of the four sample tubes. The system was purged with the gas for 15 minutes before the degradation was started.
4. The samples were heated to the desired degradation temperature at a rate of 10°C min^{-1} and held isothermally at the degradation temperature for 30 minutes.
5. Following the isothermal hold period the tubes were removed from the block heater and allowed to cool before the aluminium sample holders were removed and weighed. This allowed the percentage mass loss for each sample to be calculated.
6. The "cold-ring" type material which formed at the top of the tubes was then removed and dissolved in chloroform before being analysed by FTIR spectroscopy and GC-MS.

2.3 Analysis of the Residue

The residues which remained in the aluminium sample holder were comprised of a chloroform soluble component and a chloroform insoluble component, which will be referred to throughout this work as *tar* and *char*, respectively. In order to separate these components the residues were removed from the foil, placed in a small jar containing chloroform and this solution was subsequently filtered through pre-weighed Whatman® filter tubes with a 1 μm pore size. Pre-weighed vials were placed below the filter tubes to collect the soluble tar components whilst the chars remained in the filter tubes. The tars and chars were then left to

dry to ensure that all solvent had evaporated before the vials and filer tubes were weighed; this allowed the quantities of tar and char to be calculated as a percentage of the total residue collected at each degradation temperature. Following this the tars were analysed by FTIR spectroscopy whilst the chars were analysed by solid-state ^{13}C NMR, FTIR spectroscopy and elemental analysis.

2.4 Solid-state ^{13}C NMR

All solid-state ^{13}C NMR spectroscopy was conducted by the solid-state NMR Service at Durham University. The samples were analysed as received using a Varian VNMRS spectrometer operating at 100.56 MHz for ^{13}C using cross-polarisation with magic angle spinning (CPMAS). A 6 mm magic-angle spinning probe was employed with a spin rate of 6.8 kHz. For each sample two spectra were recorded, the first was recorded using the TOSS technique to remove any spinning sidebands from the spectra and the second was recorded using dipolar dephasing with no sideband suppression.

2.5 FTIR Spectroscopy

FTIR analysis of any cold-ring fractions (cast as thin films from chloroform onto NaCl discs), liquids and tars were carried out using a Perkin Elmer Spectrum 100 FTIR Spectrometer in transmission mode, recording 32 scans at a resolution of 4 cm^{-1} over the range 4000 - 500 cm^{-1}. FTIR analysis of the solid degradation chars was achieved by use of an A2 Technology ML FTIR with a diamond ATR cell (now an Agilent 5500a FTIR with diamond ATR cell), recording 64 scans at a resolution of 4 cm^{-1} over the range 4200 - 600 cm^{-1} . The spectra obtained from ATR-FTIR experiments are traditionally plotted as absorbance versus wavelengths, however, for the purposes of this work these have been converted to % transmittance so that all the FTIR spectra are of the same format. All spectra were background-corrected. For transmission spectra the baseline was obtained using an empty beam path rather than with the blank NaCl discs in place. Table 1 shows the spectral assignments for the FTIR peaks.

Table 1: Correlation table for the typical FTIR bands observed for polyurethanes and their degradation products

Functional Group/Compound	Formula	Band(s) (cm^{-1})	Vibration
Urethane	RNHCOOR	1740-1690 1200-1400	C=O stretching C-N stretching
Urea	RNHCONHR	1660 1200-1400	C=O stretching C-N stretching
Isocyanate	RN=C=O	2275-2250	N=C=O stretching
Aromatic groups	Ar-H	3040-3010 ~1600, ~1580, ~1500	C-H stretching C=C skeletal stretching
Alcohol (polyol)	R-OH	3600-3200 1410-1260	O-H stretching O-H bending
Alkyl Ether (polyol)	R-O-R	1150-1070	C-O-C stretch
Aliphatic groups	$-CH_3$ or $-CH_2-$ R_3-CH	2960-2850 1470-1430 2890-2880	C-H Stretching C-H deformations C-H stretching
Alkene	$R_2C=CR_2$	1680-1620 3095-3010 995-790	C=C stretching C-H stretching C-H out of plane deformations
Ketone	R-CO-R Ar-CO-R	1725-1705 1700-1680	C=O stretching C=O stretching
Aldehyde	R-CHO Ar-CHO	1740-1720 1715-1695	C=O stretching C=O stretching
Carbodiimide	RN=C=NR	2155-2130	C=N stretching
Amine	RNHR, RNH_2, ArNHR, $ArNH_2$	3500-3300 1650-1560 1200-1400	N-H stretching N-H bending C-N stretching

3. RESULTS

3.1 Non-oxidative Degradation Studies

3.1.1 Mass Loss Data and Observations

Presented in Table 2 are the residues obtained, calculated as a percentage of the original sample mass, after degradation of the foam under a nitrogen environment. The quantities of residue obtained are the averages which have been calculated from the four repeat analyses.

Table 2: Residue yields obtained for the foam after degradation under nitrogen

Degradation Temperature /°C	**Residue /% original sample mass**
250	98
300	75
350	39
400	15

Very little mass loss occurs at 250°C. There was no visible discolouration or degradation of the foam at this temperature and extraction of the sample with chloroform did not yield any tarry material. This is the temperature at which the urethane bonds within the material are reported to begin to degrade; however, these results suggest that a significant level of scission has not occurred at this temperature. This is in correlation with the results from the TGA and TVA analysis which showed that mass loss from the foam in an inert environment did not become significant until temperatures greater than 250°C [14].

As the degradation temperature was increased the foam became darker in colour and by 400°C the foam appeared black and highly charred, indicating that significant degradation of the polyurethane had occurred [see Supplementary Material Figure SM1].

3.1.2 Cold-ring Fraction Analysis

During the degradation a "cold-ring" type fraction consisting of high molar mass material which had volatilised from the sample was deposited at the top of the sample tubes. This was removed by swabbing with chloroform and analysed by FTIR spectroscopy and GC-MS. As was mentioned above, during the degradation at 250°C very little mass loss had occurred. There was, therefore, little cold-ring in the tube at this temperature and the GC-MS and FTIR spectroscopy analysis showed no significant peaks of interest. At all other temperatures a cold-ring fraction was deposited which consisted of two components: a white wax-like insoluble residue and a yellow/orange chloroform soluble residue. The FTIR spectrum of the white insoluble component of the cold-ring fractions was similar to that obtained during the TVA study [14], showing peaks consistent with a polyurea structure. This indicates that amines were also evolved during the degradation of the foam.

The FTIR spectrum of the yellow/orange chloroform-soluble component of the cold-ring fraction collected from the foam after degradation at 300°C (Supplementary Material Figure SM2) shows peaks corresponding to ether-containing fragments and aromatic amines. The aromatic amine peaks suggest that diaminotoluene may be produced during the degradation of the foam and the ether-containing fragments are likely to be higher molar mass fragments produced from degradation of the polyol component of the foam.

By 400°C the FTIR spectrum of the cold-ring fraction, presented as Supplementary Material Figure SM3, has a number of peaks which correspond to structures resembling the polyol component of the foam. In addition, a peak at 1727 cm^{-1} indicates the presence of carbonyl-containing compounds within the cold-ring. It is, therefore, proposed that by 400°C the cold-ring fraction is composed mainly of high molar mass polyol fragments, some of which contain carbonyl groups within their structure.

GC-MS analysis was also conducted on the chloroform soluble cold-ring fractions collected from the foam and complex chromatograms were obtained. Presented in Figure 1 is an example total-ion chromatogram for the foam which is representative of the cold-ring fractions collected. The large peak at a retention time of 10.33 minutes has been positively identified as diaminotoluene, whilst smaller peaks at 9.70 minutes and 9.74 minutes have been identified as 2,6-TDI and 2,4-TDI, respectively. The remainder of the peaks correspond in the most part to high molar mass polyol chain fragments sharing common m/z fragments. Due to the large number of possible products which could be derived from the polyol chain complete identification of these species was not possible. There were also a small number of peaks which could not be definitively identified but library searches suggest nitrogen-containing aromatic compounds.

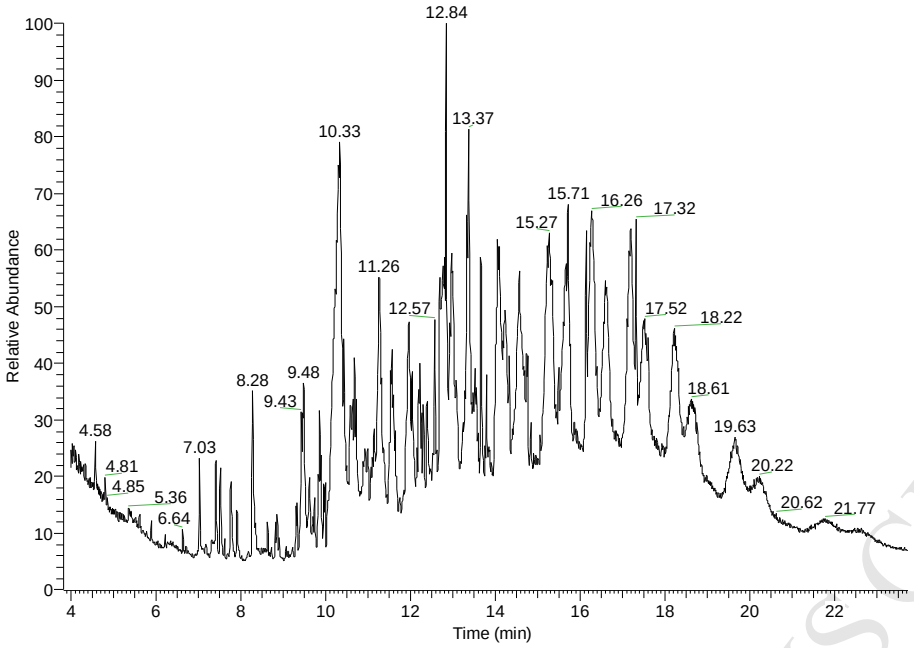


Figure 1: GC-MS total-ion chromatogram for the cold-ring fraction collected from the foam after degradation under nitrogen at 350°C

The presence of polyurea and diaminotoluene within the cold-ring fractions is significant as this gives further insight into the thermal degradation mechanisms of the foam. As has been discussed previously the urethane linkages can degrade *via* a depolymerisation reaction to yield isocyanate and polyol, or *via* six-membered or four-membered ring transition states to yield primary or secondary amines. It has been reported in many cases that the depolymerisation reaction is the predominant degradation mechanism [3, 5, 7]. However, it has been shown that if the diisocyanate cannot volatilise from the system it will become trapped within the degradation zone and the polyol and isocyanate can recombine to reform the urethane bond [2, 7]. In this situation the slower, irreversible reaction *via* a six-membered ring transition state becomes favoured and a primary amine would be produced.

The TVA studies revealed the predominant degradation mechanism of the urethane linkages within the foam to be depolymerisation to yield isocyanate and polyol [14]. The TVA technique operates under a vacuum of approximately 10^{-4} Torr and the volatiles are pumped from the degrading polymer system. The degradation studies, on the other hand, are conducted at atmospheric pressure; therefore, degradation of the sample in the degradation system occurs at pressures which are seven orders of magnitude higher compared to the TVA system. Degradation in the degradation system is, therefore, a higher pressure, more

confined situation and this will have an effect on the reactions which occur. Under vacuum it is proposed that degradation of the urethane linkages *via* the depolymerisation reaction occurs at a faster rate than the cyclic mechanism. When the depolymerisation reaction occurs to yield the monomers the high vacuum facilitates the volatilisation of the TDI into the cold-ring fraction. Loss of TDI from the degrading polymer system drives the equilibrium in the forward direction and makes it less likely for the TDI and polyol to recombine in the reverse reaction.

In the degradation experiments at atmospheric pressure diaminotoluene is observed as a major degradation product and it is proposed that the higher pressure, more confined situation changes the balance of the depolymerisation-polymerisation equilibrium such that the reverse reaction (recombination of the polyol and TDI) occurs to a greater extent than was the case under vacuum. In this situation the six-membered ring transition state mechanism, which is irreversible, then begins to dominate to yield the diaminotoluene, carbon dioxide and alkene terminated polyol chains. The higher pressure conditions, therefore, appear to have a significant effect on the mechanism by which the urethane linkages degrade, causing the usually slower, irreversible six-membered ring transition state reaction to become the predominant mechanism. This is in agreement with the work of Ravey and Pearce [2] and Erickson [26] who found that TDI-based foams yielded isocyanate when thermally degraded in an unconfined environment, although under confined conditions diaminotoluene was released in larger amounts. Ravey and Pearce also proposed that the diaminotoluene can react in the vapour phase with any isocyanate released to form a polyurea aerosol. It is, therefore, proposed that a similar reaction occurs in this system to yield the white polyurea residue observed in the cold-ring fraction.

3.1.3 Residue Analysis

The residues which remained in the aluminium sample holder were comprised of a chloroform soluble component (tar) and an insoluble component (char). These components were separated as described in section 2.3 to allow for further analyses. The tar was analysed by FTIR spectroscopy, whilst the char was characterised by elemental analysis, solid-state ^{13}C NMR and FTIR spectroscopy. No discolouration was present in the residue obtained after degradation at 250°C and extraction of this sample with chloroform did not yield any soluble component. The residues at all other temperatures yielded both tar and char.

3.1.4 Quantification of the Tar and Char

Presented in Table 3 are the quantities of char and tar calculated as a percentage of the total residue collected and char as a percentage of the original sample mass for the foam after degradation under nitrogen.

Table 3: Quantities of tar and char obtained as a percentage of the residue collected for degrdation under nitrogen, and char as a percentage of the original sample mass

Temperature /°C	**Tar /% of total residue mass**	**Char /% of total residue mass**	**Char /% of original sample mass**
250	0	100	100
300	82	18	14
350	71	29	12
400	40	60	9

Under nitrogen, at 250°C there was no tar collected and the residue consisted entirely of insoluble material. This was not unexpected as the previous results have shown that very little degradation had occurred at this low a temperature. It can be observed that the sample degraded at 300°C produced significantly more tar than char, and as the degradation temperature was increased the level of tar within the residue began to decrease as the foam became more charred in nature. The tar is comprised of the chloroform soluble components of the residue and is expected to primarily contain regenerated polyol or polyol-based material. The level of tar was, therefore, expected to decrease as the degradation temperature increased due to degradation and volatilisation of the polyol component.

3.1.5 Analysis of the Tar

Presented in Figure 2 is the FTIR spectrum for the tar obtained from the foam after non-oxidative degradation at 300°C.

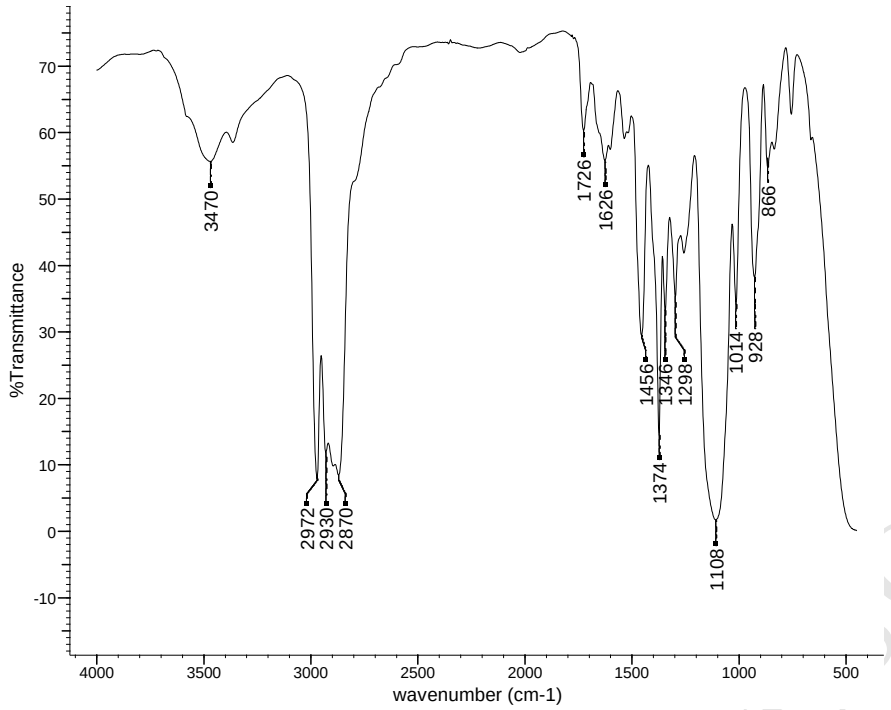


Figure 2: FTIR spectrum of the tar extracted from the foam after degradation at 300°C under nitrogen

The majority of the peaks are associated with structures which resemble the polyether polyol component of the foam; this is confirmed by comparison with the FTIR spectrum of the pure polyol (Supplementary Material, Fig SM6). The spectra are almost identical; however, there are peaks in the FTIR spectrum of the tar which are not present in the polyol spectrum. In particular, the peaks at 1626 cm^{-1} and 928 cm^{-1} indicate that unsaturation is present whilst the peak at 1726 cm^{-1} indicates the presence of carbonyl groups within the tar. This suggests that the tar does not simply consist of regenerated polyol but instead consists of polyol which has degraded to some extent. This is confirmed by the appearance of the tar which is brown in colour whereas the undegraded polyol is colourless. The carbonyl groups could be present due to degradation of the polyol; however, they could also be carbonyl groups within urethane linkages which would suggest that some residual urethane links are present within the tar at 300°C.

The presence of C=C peaks is significant as this gives further insight into the mechanisms by which the urethane linkages are degrading. As was discussed previously, degradation of the urethane linkage by a six-membered ring mechanism would yield an amine as the major degradation product instead of the isocyanate. If this was the case, then the residue which

remained would resemble the polyol but with an unsaturated end group. The presence of unsaturation within the tar, therefore, supports the earlier proposal that under confined degradation conditions the foam is undergoing thermal degradation primarily *via* a six-membered ring transition state to yield diaminotoluene, CO_2 and alkene terminated polyol chains. This is once again in contrast to the results obtained when the foam was degraded under the less confined conditions of TVA.

The FTIR spectra of the tars collected from the foam at 350°C and 400°C showed no major differences compared to that at 300°C which indicates that although the quantity of tar decreases as the temperature is increased, the structure remains similar.

3.1.6 Analysis of the Char - Solid-state ^{13}C NMR

Presented in Figure 3 are the ^{13}C CPMAS TOSS spectra for the virgin foam and the chars obtained from the foam after degradation at 250, 300, 350 and 400°C.

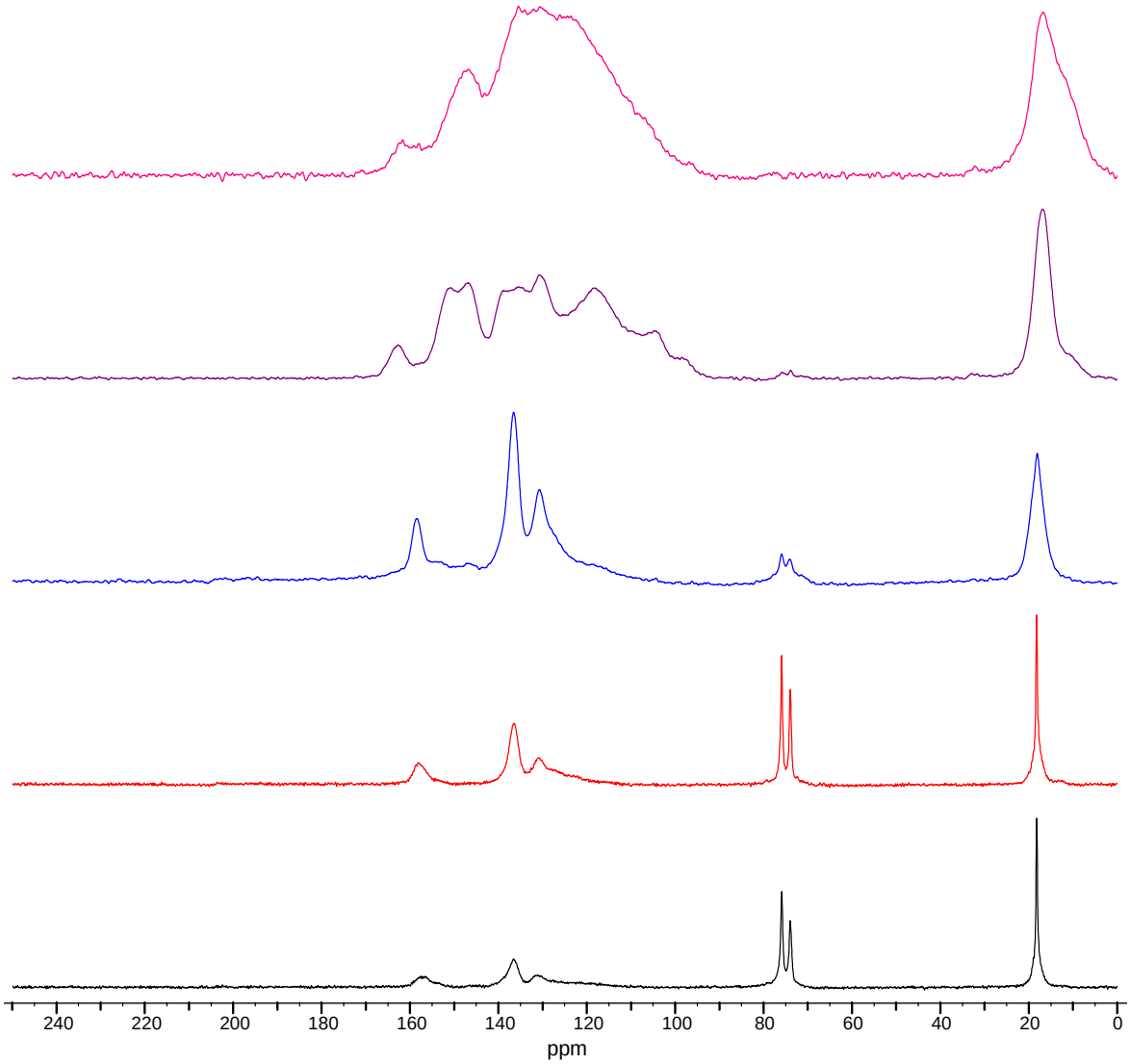


Figure 3: Comparison of the ^{13}C CPMAS TOSS spectra of the virgin foam (black, lowest) with the chars obtained after degradation under nitrogen at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink, uppermost)

For the virgin foam, the signals between 110 and 160 ppm arise from the aromatic and urethane carbons and are broad, which is typical of a rigid or hard component in a polymeric material. The narrower signals between 70 and 80 ppm are indicative of a soft component which has more molecular mobility; therefore, these peaks can be assigned to the aliphatic carbons within the polyol component of the polyurethane. The signal at 18.2 ppm arises from methyl carbons and appears as a composite peak as there are two sources of methyl group: the methyl groups within the poly(propylene glycol) segments of the polyol and the methyl groups of the TDI component.

The spectrum of the 250°C residue is similar to the virgin foam with all the original signals present. This confirms that no significant degradation of the polyurethane has occurred at this temperature and that a significant number of urethane linkages are still present within the foam. By 300°C the polyol signal is significantly reduced which suggests that significant degradation of the urethane linkages has occurred by this temperature. This correlates well with the results from the tar analysis which revealed that a large quantity of polyol-based tar had been produced at 300°C. As the level of polyol present has decreased significantly at this temperature, the peak at 18 ppm will be expected to now be largely due to the methyl groups of the TDI component. The broadness of this peak suggests that this is the case as a broader peak indicates a methyl group with more restricted mobility.

The spectrum of the char from the 350°C degradation is considerably different to those at the lower temperatures and indicates a change in the structure of the char at this temperature. The polyol signal has almost disappeared by this temperature and there is a significant change in the high chemical shift region of the spectrum. There are several peaks now observed between 110 to 170 ppm which indicates a number of aromatic carbons in different chemical environments, suggesting that the char has a complex aromatic structure at this temperature. Furthermore, the signal from the methyl group has become broader suggesting more restricted mobility of this component.

By 400°C no polyol peaks are observed in the char, the methyl signal is even broader still and the peaks in the high chemical shift region are poorly resolved. This suggests that by this temperature the foam which remains is highly charred, as is evident in the photographs presented in Supplementary Material Figure SM4, and that this char consists entirely of aromatic structures which are complex in nature.

Displayed in Figure 4 are the ^{13}C CPMAS dipolar dephased spectra for the virgin foam and the chars obtained from the foam after degradation at 250, 300, 350 and 400°C. In these spectrum the label * is used to denote the spinning sidebands as they were recorded without suppression of sidebands.

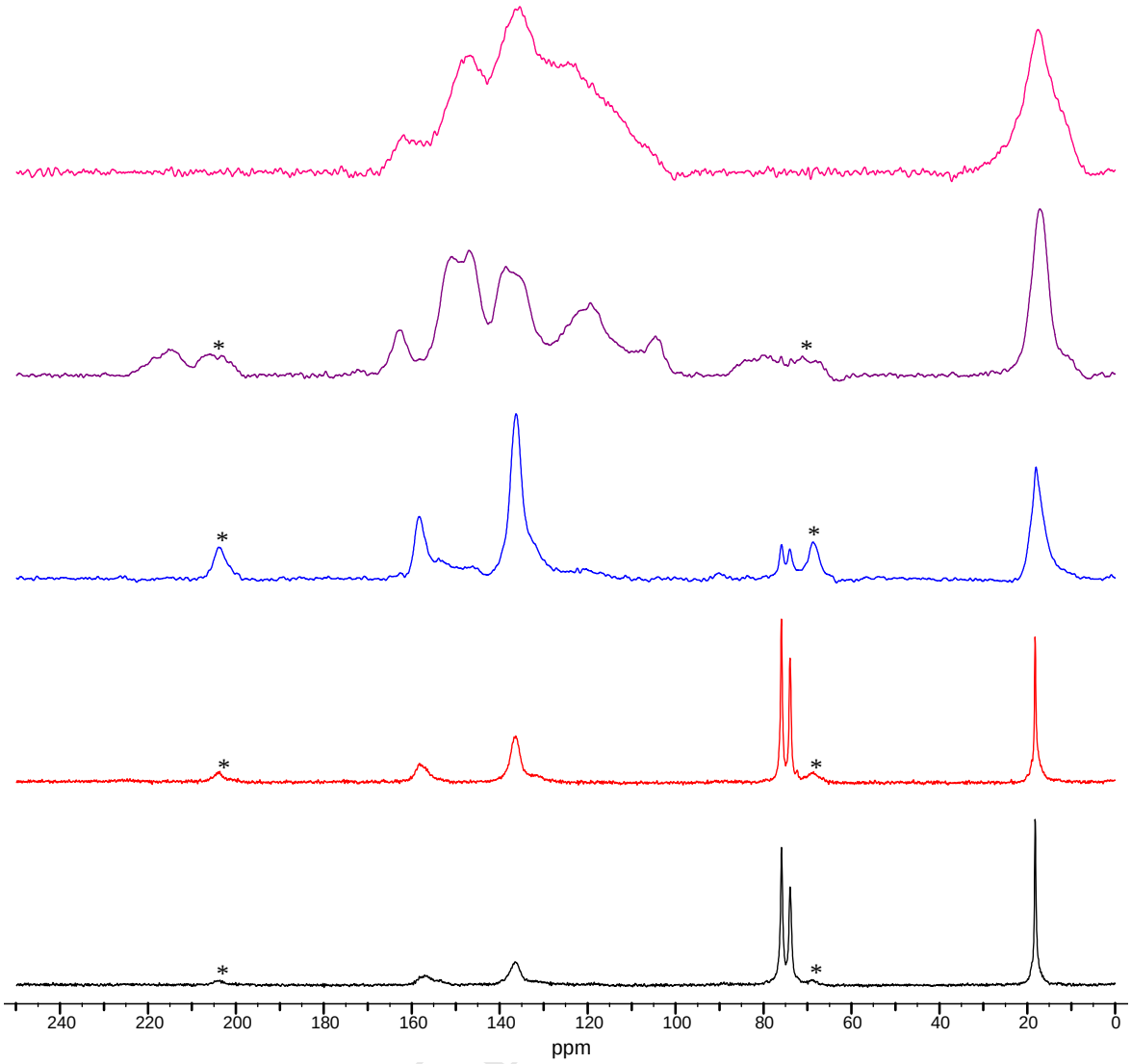


Figure 4: Comparison of the ^{13}C CPMAS dipolar dephased spectra of the virgin foam (black, lowest) with the chars obtained after degradation under nitrogen at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink, uppermost)

Dipolar dephasing is employed as it suppresses the signals originating from protonated carbons, therefore, it can provide further information regarding the structure of any chars which form. For the virgin foam, all of the signals detected in the TOSS spectrum remain after dipolar dephasing apart from the signal at 131 ppm. This arises from the protonated aromatic carbons of the TDI component within the foam and is, therefore, suppressed by the dipolar dephasing. The signals at 157.1 and 136.5 ppm remain as these correspond to the unprotonated urethane carbons and the quaternary aromatic carbons, respectively. This technique does not, however, suppress species with a high degree of molecular mobility and, as a consequence, the peak corresponding to the methyl carbons at 18.2 ppm is retained. The

peaks arising from the protonated polyol carbons at 73.9 and 75.9 ppm are also retained which confirms that this component has a high degree of mobility.

The spectra from the 250°C and 300°C residues exhibit the same characteristics as the TOSS spectra, showing loss of polyol with retention of the aromatic species within the char. The high chemical shift region of the dipolar dephased spectrum from the 350°C residue is similar to that of the TOSS spectrum at this temperature, which indicates that the majority of the carbons contributing to the signal are unprotonated. This is also the case for the spectrum for the 400°C residue, and this confirms that the char generated at the higher temperatures is aromatic and that a considerable quantity of this is unprotonated. This suggests that a significant amount of ring fusion has occurred at the higher temperatures generating a complex char structure which consists of a number of aromatic species.

3.1.7 Analysis of the Char - FTIR Spectroscopy

Presented in Figure 5 are the FTIR spectra for the virgin foam and the chars obtained from the foam after degradation under nitrogen at 250, 300, 350 and 400°C. Comparison of the undegraded foam spectrum with that of pure polyol reveals that the majority of the peaks in the spectrum arise from the polyol component of the foam; however, there are additional peaks of importance. The peaks at 1729 and 1226 cm^{-1} are due to the urethane linkages, whilst the peaks between 1500 and 1650 cm^{-1} correspond to the aromatic segments of the foam. The peak at 3294 cm^{-1} is likely due to the N-H stretching of the urethane linkages and any urea linkages which may be present. The small peak at 2274 cm^{-1} suggests the presence of a small quantity of unreacted isocyanate groups within the foam.

The spectrum from the sample degraded at 250°C is similar to the virgin foam with the only difference being the absence of the peak at 2274 cm^{-1} corresponding to residual isocyanate groups, which indicates that unreacted isocyanate groups are no longer present at 250°C. The peaks corresponding to the urethane linkages are still present which suggests that a significant number of urethane linkages remain in the foam at this temperature. These results are consistent with the solid-state ^{13}C NMR results and confirm that there has been no significant degradation of the polyurethane at 250°C. By 300°C the urethane carbonyl peak at 1729 cm^{-1} is small and the polyol peaks are no longer as dominant in the spectrum. This indicates that significant degradation of the urethane linkages has occurred by this temperature, which is in agreement with the results presented previously.

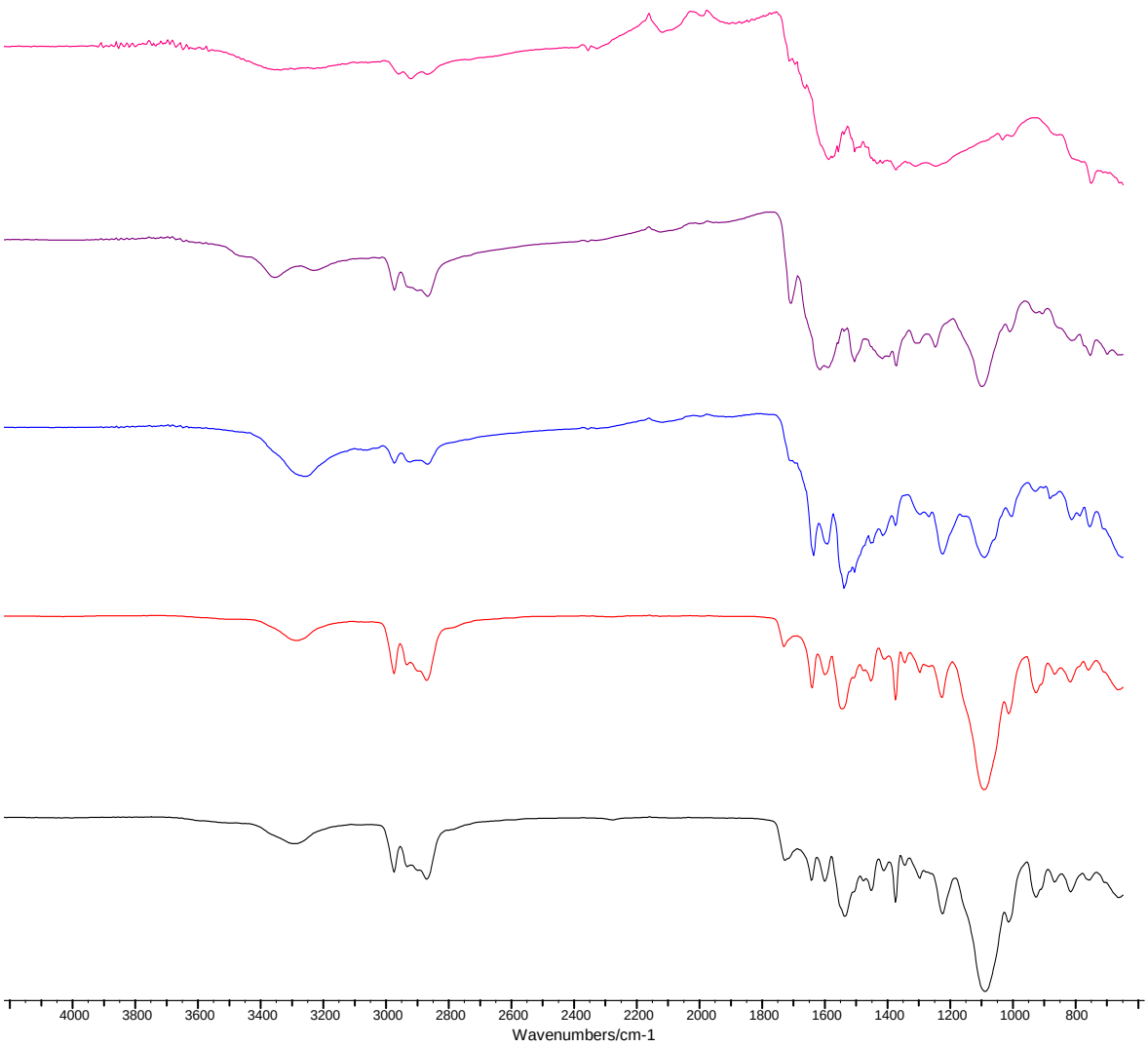


Figure 5: Comparison of the FTIR spectra of the virgin foam (black, lowest) with the chars obtained after degradation under nitrogen at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink, uppermost)

From the 350°C residue, there are still weak polyol peaks present, as was the case in the solid-state NMR, and a new carbonyl peak is now present at 1710 cm^{-1}. This suggests that any polyol remaining in the char has now begun to degrade yielding carbonyl-containing structures. There is now much less of a signal present from the hydroxyl groups of the polyol component of the foam and a second peak around 3350 cm^{-1} can now be observed, which suggests the presence of aromatic amines within the char. The previous results suggested that DAT is a major degradation product arising from the degradation of the foam; therefore, it could be the case that this undergoes secondary reactions and is incorporated into the char at 350°C.

By 400°C the foam is highly charred and the FTIR spectrum is unstructured and difficult to interpret, which confirms that the char is carbonaceous in nature.

3.1.8 Analysis of the Char - Elemental Analysis

The results from the elemental analysis are reported in Table 4.

Table 4: Elemental analysis results for the virgin foam and the degradation chars

Degradation Temperature /°C	**%C**	**%H**	**%N**	**C/H**	**C/N**
Virgin	61.7	9.1	5.3	6.8	11.6
250	61.9	9.2	5.0	6.7	12.4
300	64.0	6.6	13.4	9.7	4.8
350	64.8	6.2	14.7	10.4	4.4
400	69.4	4.8	12.3	14.4	5.6

At 250°C the C:H and C:N ratios are not significantly different to those of the virgin foam indicating that very little degradation has occurred at this temperature. This is in agreement with the data presented thus far. The C:H ratio is then observed to significantly increase between 250°C and 300°C which suggests loss of polyol has occurred. This is again in agreement with the previous results which demonstrated that by 300°C significant degradation of the urethane linkages has occurred to yield a polyol-based tar and an aromatic char. Between 350°C and 400°C the C:H ratio significantly increases once again which correlates well with the solid-state ^{13}C NMR results which suggests that at these higher temperatures significant ring fusion of the aromatics occurs to yield a complex, highly unprotonated carbonaceous char.

The C:N ratio, on the other hand, decreases between 250°C and 350°C which indicates that as the polyol is lost from the system, a large proportion of the nitrogen from the urethane linkages remains within the char. This is in agreement with the FTIR results which showed the presence of aromatic amine species within the char at 350°C. This suggests that in the confined environment of the degradation the nitrogen-containing species (*e.g.* TDI and

diaminotoluene) undergo secondary reactions and, as a result, a large proportion of the nitrogen-containing species become incorporated into the char. Calculation of the quantity of nitrogen in the char as a percentage of the nitrogen present in the virgin foam reveals that approximately 22% of the original nitrogen present in the foam remains within the char after degradation at 400°C. The quantity of original carbon remaining, on the other hand, is 11%. This indicates that the nitrogen-containing species are preferentially retained within the char as the polyol is lost from the system. This is expected as the char has been shown to be mostly aromatic in nature, with the aromatic units within the foam deriving from the isocyanate.

3.2 Oxidative Degradation Studies

3.2.1 Mass Loss Data and Observations

The residues obtained, calculated as a percentage of the original sample mass, after degradation of the TDI foam under air are presented in Table 5. Photographs of the chars collected from the standard foam after degradation under air, which were significantly different to those obtained under nitrogen are shown in Supplementary Material Figure SM4. The char obtained at 250°C under air resembled the char at 300°C under nitrogen, being brown in colour and having lost some of the foamed structure. By 300°C under air the char was already blackened and powdery, having lost all of its original foamed structure. The chars at 350°C and 400°C were similar in appearance.

Table 5: Mass losses and residues for the TDI foam after degradation under air

Degradation Temperature / °C	**Residue / % original sample mass**
250	95
300	47
350	27
400	18

An increase in mass loss and decrease in the quantity of residue is observed as the degradation temperature increases. This is indicative of increased levels of degradation at the higher temperatures, which leads to larger quantities of volatile material being evolved. At 250°C discolouration of the foam had occurred, indicating that degradation had occurred to some extent at this temperature but the corresponding mass loss is relatively small indicating

that the products formed during the degradation have not volatilised to any great extent or undergone secondary reactions to produce volatile degradation products. As the degradation temperature was increased the extent of degradation will have increased and it can be observed from Table 2 that the greatest mass loss occurred between 250°C and 300°C. This indicates that significant quantities of volatile degradation products have been evolved from the sample in this temperature range, and it is proposed that this occurs as a result of thermo-oxidative degradation of the polyol component of the foam.

It is clear that there are no significant differences in the mass losses under air or nitrogen at 250°C. However, above this temperature the mass loss is clearly accelerated in air. It has been reported that the presence of oxygen does not significantly influence the primary degradation step of the polyurethane [19, 20] and the results presented in Tables 2 and 5 suggest that this is indeed the case for the foam. It has also been reported that the soft segments of the polyurethane, *i.e.* the polyol chains, are more susceptible to oxidative degradation than the hard segments [18]. It is, therefore, proposed that above 250°C thermo-oxidative degradation of the polyol segments within the foam occurs, producing a large quantity of volatile degradation products. Thermo-oxidative degradation of the polyol is expected to occur at lower temperatures than purely thermal degradation [15], therefore, increased mass loss is observed at lower temperatures relative to the degradation under nitrogen. This is in correlation with a number of studies published on the degradation of polyurethanes or their constituents [1, 27, 28].

3.2.2 Cold-ring Fraction Analysis

In contrast to the pyrolyses under nitrogen, a yellow cold-ring fraction was obtained at all temperatures during the degradation under air, although only a small quantity was present at 250°C. This again indicates that degradation of the polyurethane is accelerated in the presence of oxygen, correlating with the mass loss data and observations discussed previously. In addition, white polyurea residue was not observed during the degradation under air. The FTIR spectrum of the cold-ring fraction at 250°C (Supplementary Material Figure SM5) indicates the presence of structures containing ether, carbonyl and hydroxyl groups. These are, therefore, likely to be higher molar mass fragments produced from the thermo-oxidative degradation of the polyol component of the foam.

GC-MS analysis was also conducted on the cold-ring fraction at 250°C and a complex chromatogram was obtained which is presented in Figure 6. The peaks of interest in the chromatogram correspond in the most part to high molar mass polyol chain fragments which share common m/z fragments. Due to the large number of possible products which could be derived from the polyol chain complete identification of these species is not possible, however, the library searches suggest the presence of cyclic species derived from the polyol such as dioxane-type structures. At this temperature TDI and DAT were not identified in the cold-ring fraction.

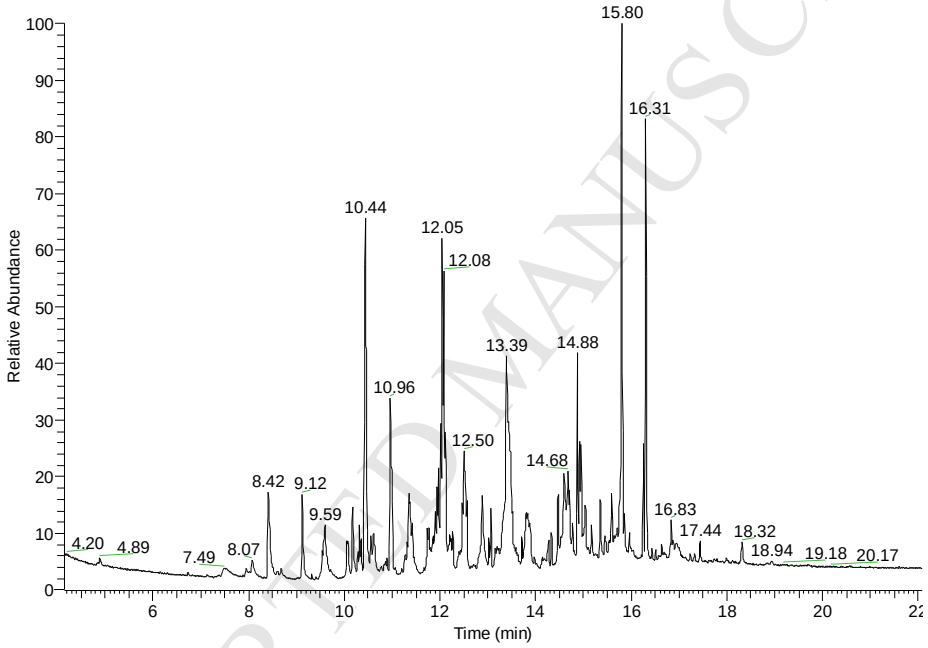


Figure 6: GC-MS total-ion chromatogram for the cold-ring fraction collected from the foam after degradation under air at 250°C

The GC-MS and FTIR spectroscopy results, therefore, indicate that the cold-ring fraction at 250°C consists primarily of polyol fragments. This confirms that at 250°C thermo-oxidative degradation of the polyol component has occurred to some extent; however, this is not likely to have reached its maximum rate at this temperature as the mass loss observed is only 5%. These results also confirm that thermo-oxidative degradation of the polyol occurs at a lower temperature than thermal degradation, as there was no polyol-based cold-ring fraction collected at 250°C during the degradation under nitrogen.

The cold-ring fractions collected at 300, 350 and 400°C were similar to that collected at 250°C, consisting primarily of high molar mass polyol fragments. TDI and DAT were not identified in any of these cold-ring fractions.

Analysis of the cold-ring fractions, therefore, indicates that thermo-oxidative degradation of the polyol component of the foam occurs at temperatures as low as 250°C and yields higher molar mass polyol fragments. The absence of the white polyurea residue which was observed during the degradation of the foam under nitrogen suggests that amines, in particular DAT, are not released during the degradation of this foam. DAT arises from degradation of the urethane linkage *via* a six-membered ring transition state; however, this mechanism is proposed to be predominant only under confined conditions when the TDI and polyol released from the depolymerisation reaction become trapped in the degradation zone and recombine. The results presented so far, however, demonstrate that under an oxidative environment the polyol undergoes oxidative degradation at a much lower temperature than in an inert atmosphere. Oxidation of the polyol will limit the likelihood of the recombination chemistry and extensive oxidative scission will also tend to lead to the volatilisation of polyol fragments from the degradation zone. In either case, polyol is not available for recombination with the TDI.

The GC-MS analysis revealed that TDI was also absent from the cold-ring fractions and it is likely that this undergoes secondary degradation reactions under an oxidative environment. This would again prevent recombination of the polyol and the TDI.

3.2.3 Residue Analysis

The residues obtained from the degradation under air yielded both tar and char at all temperatures. This is in contrast to the degradation under nitrogen which yielded no tar at 250°C and confirms that degradation of the polyurethane is altered in the presence of oxygen. The tars were analysed by FTIR spectroscopy, whilst the chars were characterised by elemental analysis, solid-state ^{13}C NMR and FTIR spectroscopy.

3.2.4 Quantification of the Tar and Char

Presented in Table 6 are the quantities of tar and char, as a percentage of the total residue, collected from the foam after degradation under air. It can be observed that the sample at

250°C produced a significant quantity of tar which confirms that degradation of the polyurethane has begun to occur at this temperature. As was mentioned previously, it has been reported that the soft segments of the polyurethane are more susceptible to oxidative degradation than the hard segments [18]. It is, therefore, likely that the tar at 250°C originates from thermo-oxidative scission of the soft segments within the polyurethane. The corresponding mass loss at this temperature was, however, relatively small and only a small quantity of cold-ring fraction was obtained. This indicates that whilst scission of the polyol chains to yield tar has occurred, the tar has not begun to degrade sufficiently to yield volatile material at this temperature.

Table 6: Quantities of tar and char obtained as a percentage of the total residue collected and char as a percentage of the original sample mass after degradation in air.

Temperature/°C	**Tar / % of total residue mass**	**Char / % of total residue mass**	**Char /% of original sample mass**
250	36	64	61
300	16	84	40
350	14	86	25
400	1	99	18

As the degradation temperature was increased, the level of tar within the residue decreased as the foam became more charred in nature, which is likely to be a result of thermo-oxidative degradation of the tar at the higher temperatures. The foam consisted almost entirely of char by 400°C. Comparison of the percentages of tar and char in the residues obtained from the pyrolyses under nitrogen (Table 3) and air reveals that the residues under air are contain more charat all temperatures, which indicates that the presence of oxygen has altered the degradation of the foam leading to char being formed at lower temperatures. Comparison of the quantities of char as a percentage of the original mass of foam confirms that the oxidative environment leads to a significantly increased level of char relative to non-oxidative degradation.

3.2.5 Analysis of the Tar

Presented in Figure 7 is the FTIR spectrum for the tar obtained from the foam at 250°C. As was the case for the tars collected under nitrogen, the majority of the peaks are associated with structures which resemble the polyether polyol component of the foam; this is confirmed by comparison with the FTIR spectrum of the polyol as shown in Supplementary Material Figure SM6.

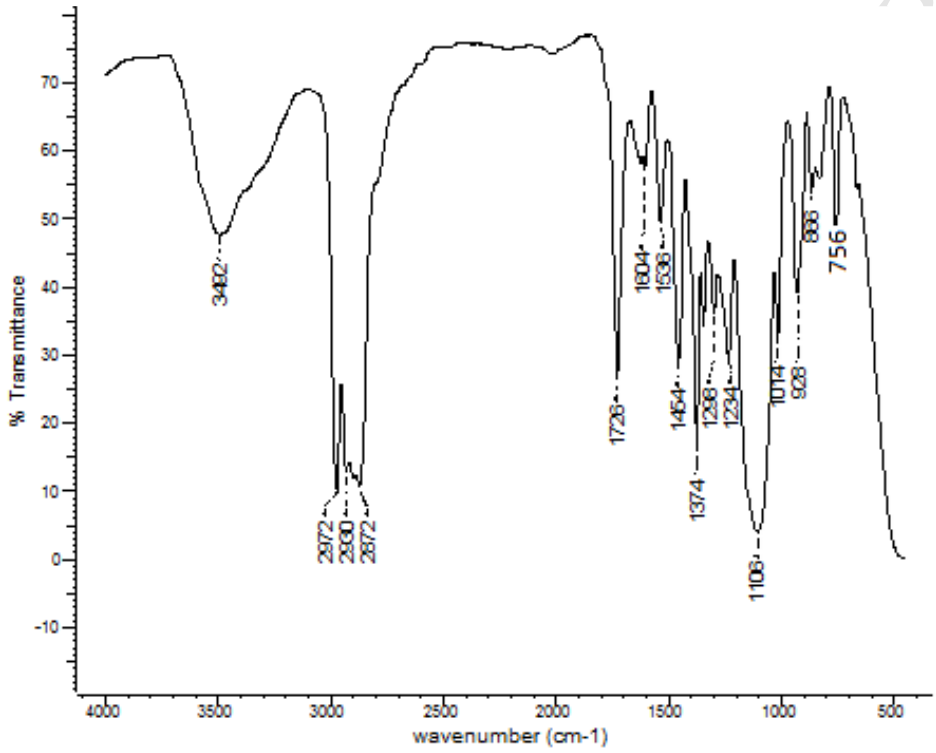


Figure 7: FTIR spectrum of the tar extracted from the foam after degradation at 250°C under air

The spectra are almost identical; however, there are additional peaks in the FTIR spectrum of the tar. The peaks at 1536 and 1604 cm^{-1} are present in the virgin foam but not the polyol (See Supplementary Material Figure SM7) and are due here to the presence of some aromatic fragments from the MDI component). The major difference, however, is the peak at 1726 cm^{-1} which indicates the presence of carbonyl groups within the tar. These carbonyl groups could be due to residual urethane bonds present within the tar but the peak is disproportionately strong relative to the peaks at 1536 and 1604 cm^{-1} and is therefore, in large measure, a result of thermo-oxidative degradation of the polyol. A peak at 756 cm^{-1} is residual chloroform from the extraction of the tar (Section 2.3). The presence of a large quantity of polyol-based tar at 250°C, which was absent during the degradation under

nitrogen, confirms that degradation of the soft segments of the foam occurs at a lower temperature in the presence of oxygen consistent with the accepted mechanism [15].

At 300°C and 350°C the peaks at 1726 and 1234 cm^{-1} became progressively smaller indicating either loss of the residual urethane linkages or loss of a carbonyl-containing polyol fragment due to further thermo-oxidative degradation of the tar. At these temperatures the FTIR spectra indicate that the tars consist mostly of regenerated polyol. By 400°C very little tar remains and the FTIR spectrum is weak, suggesting significant thermo-oxidative degradation of the polyol has occurred by this temperature.

3.2.6 Analysis of the Char - Solid-state ^{13}C NMR

Presented in Figure 8 are the ^{13}C CPMAS TOSS spectra for the virgin foam and the chars obtained from the foam after degradation at 250, 300, 350 and 400°C under air. The peak assignments for the virgin foam are the same as those discussed previously. The spectrum at 250°C is similar to the virgin foam with all the original signals still being present; however, there is a decrease in the intensity of the polyol peaks at 73.9 and 75.9 ppm relative to the aromatic peaks between 110 and 170 ppm. The methyl peak at 18.2 ppm is also broader at this temperature which indicates that less of a signal is present from the more mobile methyl groups of the polyol. This indicates that a significant quantity of the polyol component has been lost from the char at 250°C, which is in agreement with the results from the tar analysis which revealed that a large quantity of polyol-based tar was extracted at this temperature. When compared to the spectrum at 250°C under nitrogen, this confirms that the presence of oxygen has caused scission of the soft segments of the foam at this temperature.

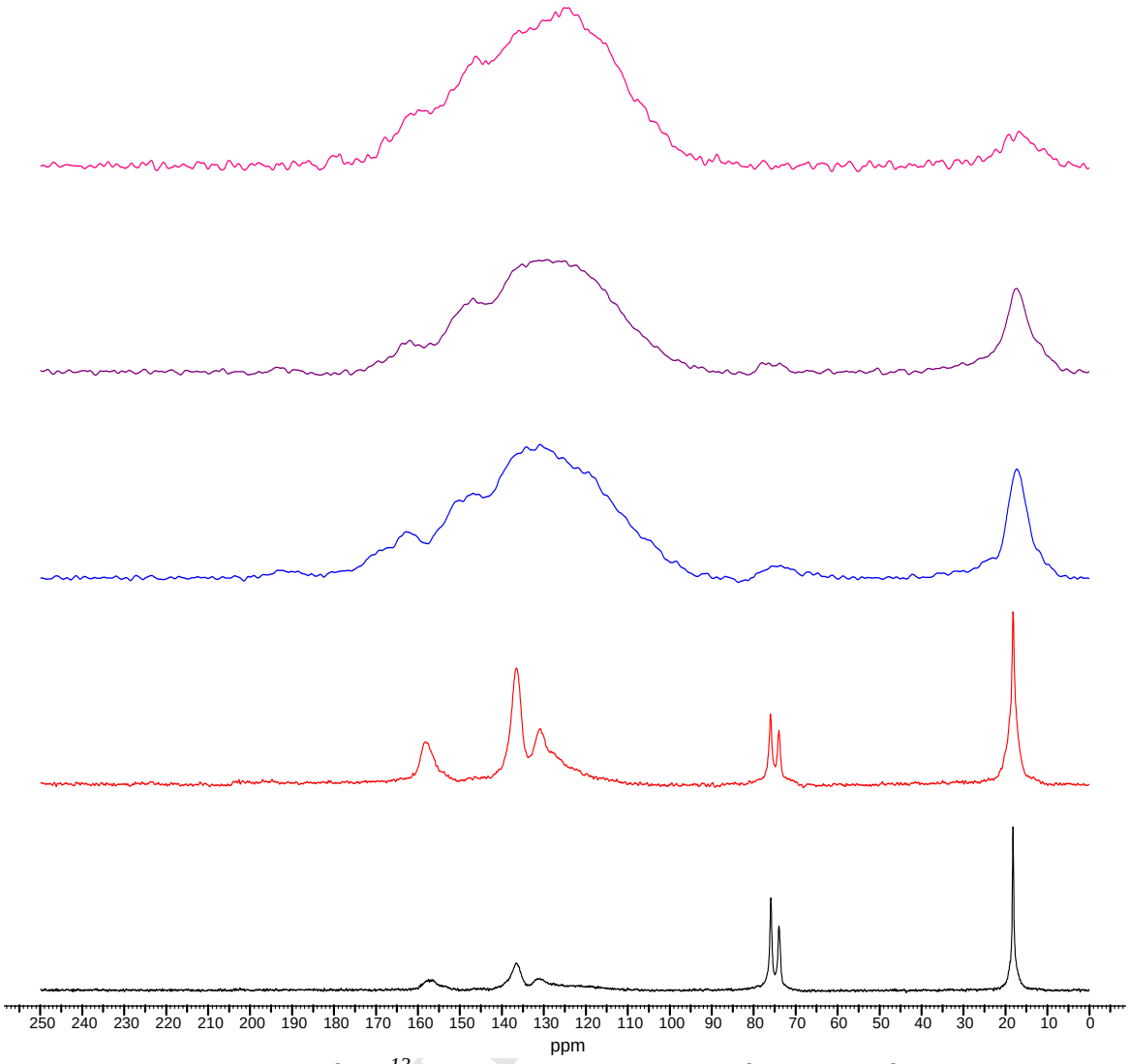


Figure 8: Comparison of the ^{13}C CPMAS TOSS spectra of the virgin foam (black) with the chars obtained after degradation under air at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink)

The spectrum of the char at 300°C is considerably different to that at 250°C and indicates a change in the structure of the char at this temperature. The peaks are much broader and less well-defined than in the corresponding spectra for samples degraded under nitrogen (Figure 6) indicating the dominance of more cross-linked and hence less mobile structures. Almost complete loss of the polyol is observed at this temperature (note the marked drop in relative intensity of the peaks 70 - 80 ppm in comparison to the corresponding spectrum in Figure 3). The broad signal at 18.2 ppm, which indicates a methyl group with more restricted mobility, is now almost entirely due to the methyl groups of the TDI component. The spectrum under air also shows a significant change in the high chemical shift region of the spectrum compared to the 250°C spectrum. There appears to be a number of signals between 110 and

170 ppm which are broad and poorly resolved. For example the peak at 157 ppm is still visible, indicating the continuing presence of urethane links but is much more poorly resolved than in the corresponding spectrum in Figure 3. This suggests the foam is highly cross-linked by this temperature and that the char consists of complex aromatic structures of limited mobility. This is in stark contrast to the residue obtained under nitrogen at this temperature and demonstrates that the degradation under air is significantly accelerated compared to the degradation under nitrogen.

The spectrum for the char at 350°C shows little difference to that at 300°C, indicating that the structure does not alter significantly between these temperatures. By 400°C, however, the high chemical shift region of the spectrum is even less resolved and the methyl signal at ~18 ppm is almost completely lost. Under nitrogen at this temperature, however, a large methyl peak was still observed. This may suggest that at the higher temperatures under air, rather than remaining as a pendant group on the aromatic system, the carbon of the methyl group gets incorporated into the aromatic structures during the ring fusion reactions. Alternatively, under an oxidative environment the aromatic components of the char may undergo reactions which lead to loss of the methyl group. Servay *et al*. [29] reported that the central methylene group in MDI undergoes oxidative reactions; therefore, it could be the case that the methyl groups in TDI undergo similar oxidative reactions at the higher temperatures. It could also be the case that scission of the methyl group causes this to be lost as methane.

The ^{13}C CPMAS dipolar dephased spectra for the virgin foam and the chars obtained under air are presented in Figure 9.

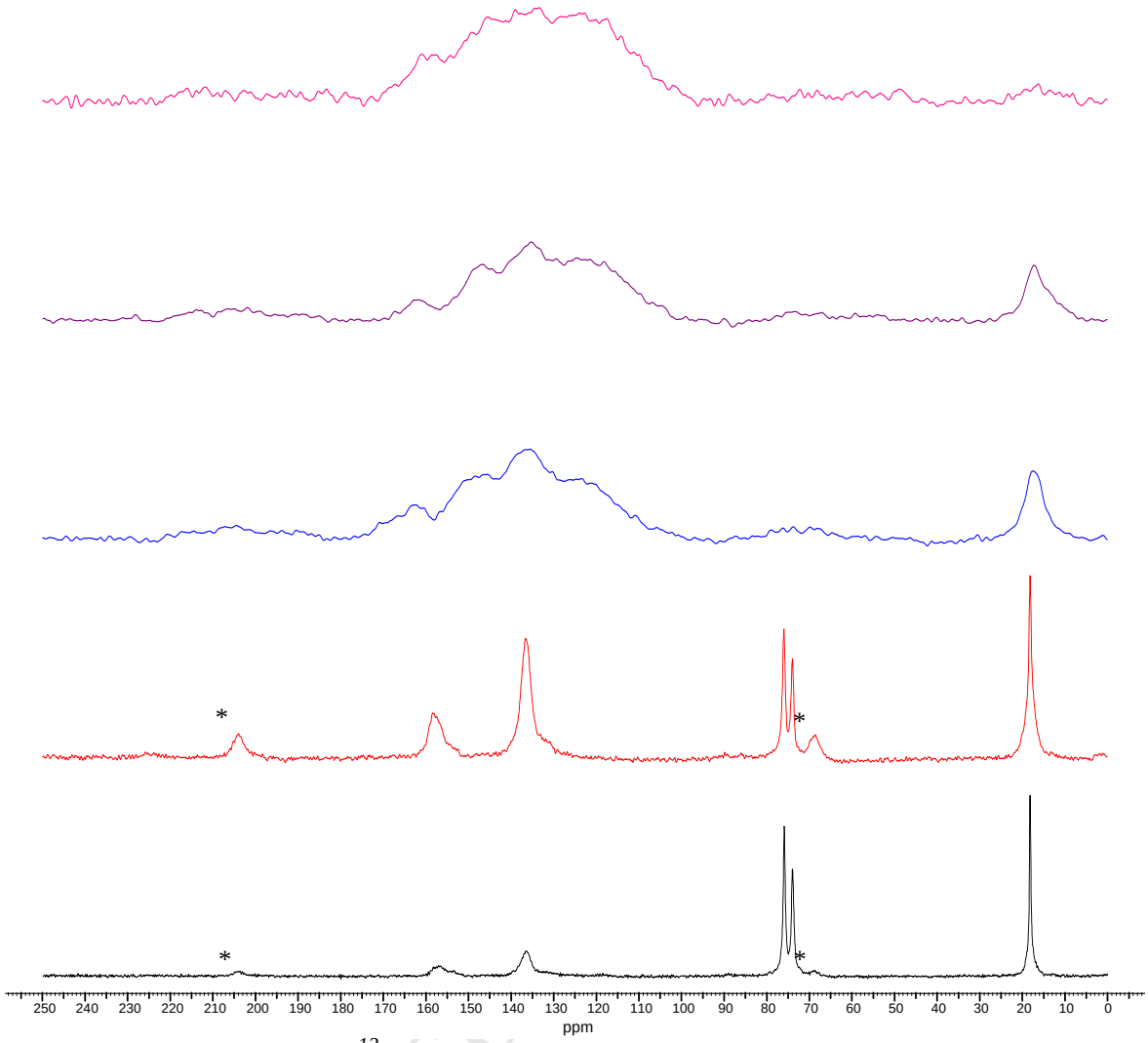


Figure 9: Comparison of the ^{13}C CPMAS dipolar dephased spectra of the virgin foam (black) with the chars obtained after degradation under air at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink)

The dipolar dephased spectra do not show significant differences to the TOSS spectra, which indicates that the majority of carbons contributing to the signal from 300°C onwards are unprotonated. This confirms that the char generated at these temperatures is aromatic and unprotonated, suggesting that a significant amount of ring fusion has occurred to generate a highly complex char structure consisting of aromatic species.

3.2.7 FTIR Spectroscopy

Presented in Figure 10 are the FTIR spectra for the virgin foam and the chars obtained from the foam after degradation under air at 250, 300, 350 and 400°C.

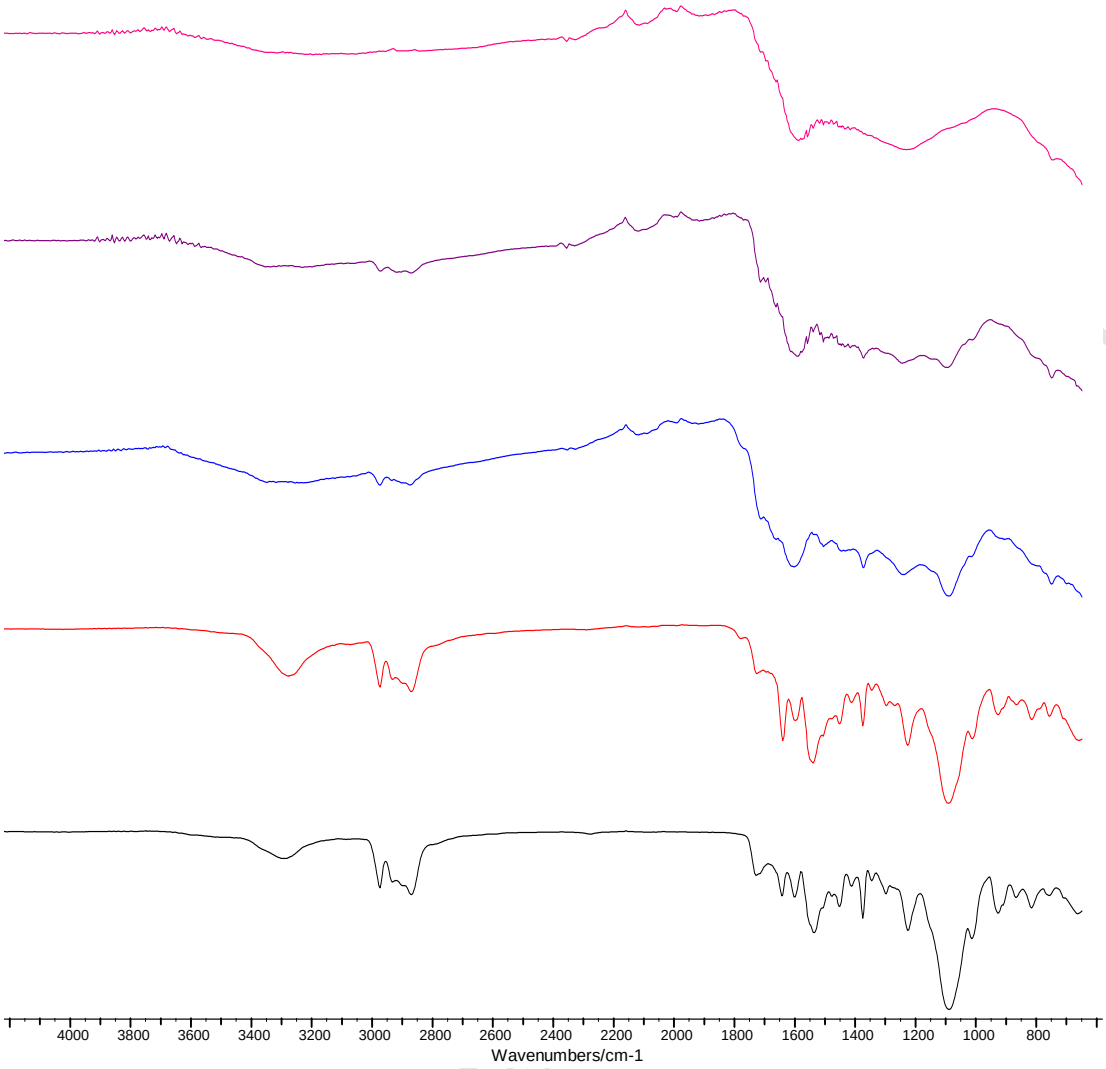


Figure 10: Comparison of the FTIR spectra of the virgin foam (black) with the chars obtained after degradation under air at 250°C (red), 300°C (blue), 350°C (purple) and 400°C (pink)

The spectrum at 250°C is similar to the virgin foam with the peak at 1729 cm^{-1} corresponding to the urethane linkages still present, which indicates that significant degradation of the urethane linkages has not occurred at this temperature. By 300°C the FTIR signals are weak and difficult to interpret. This indicates that the foam is already highly charred and carbonaceous by this temperature, which is in correlation with the previous results. The urethane carbonyl peak at 1729 cm^{-1} is significantly reduced which indicates that significant degradation of the urethane linkages has occurred by 300°C. The spectrum at 300°C under air closely resembles that at 400°C under nitrogen which once again indicates that the degradation of the polyurethane foam is accelerated in the presence of oxygen. The spectra for the chars at 350°C and 400°C are weaker still, indicating further charring of the foam at

these temperatures. No further information could be gained from these spectra due to the charred nature of these samples.

3.2.8 Elemental Analysis

The virgin foam and the chars from the degradation under air were submitted for elemental analysis to determine the percentages of carbon, hydrogen and nitrogen which were present as this may provide more information regarding the structure of the chars. The results are presented in Table 7.

Table 7: Elemental analysis results for the virgin foam and the degradation chars under air

Degradation Temperature /°C	**%C**	**%H**	**%N**	**C/H**	**C/N**
Virgin	61.7	9.1	5.3	6.8	11.6
250	62.2	7.4	8.7	8.4	7.1
300	60.3	4.2	11.4	14.4	5.3
350	67.4	4.7	10.5	14.3	6.4
400	65.2	3.0	13.6	21.7	4.8

At 250°C the C:H ratio increases relevant to the virgin foam which indicates that loss of polyol has occurred. This is in agreement with the data presented previously which indicated that thermo-oxidative degradation of the soft segments had occurred by this temperature, with the extraction of a large quantity of polyol-based tar and a decrease in the intensity of the polyol signals within the solid-state NMR ^{13}C. This is, however, in contrast to the results obtained under nitrogen which showed no significant differences between the C:H ratios of the virgin foam and the char at 250°C, which again confirms that the degradation of the soft segments is altered in the presence of oxygen.

The C:H ratio then increases even more significantly between 250°C and 300°C which indicates further loss of the polyol at this temperature. This is in correlation with the solid-state ^{13}C NMR results which showed almost complete loss of polyol by 300°C. Between 350°C and 400°C the C:H ratio increases once again which suggests loss of a hydrogen rich component between these temperatures. Almost complete loss of the methyl group was observed in the solid-state ^{13}C NMR at 400°C and one suggestion for this occurrence was

loss of the methyl group in the form of methane. This would explain the increase in the C:H ratio at 400°C.

The C:N ratio, on the other hand, decreases significantly at 250°C compared to the virgin foam, and again between 250°C and 300°C. This indicates that a large quantity of the nitrogen-containing components of the foam remain within the char when the polyol-based tar is lost from the system. As was the case under nitrogen, this suggests that under the confined conditions of the degradation the nitrogen-containing species, such as TDI, may undergo secondary reactions which lead to a large proportion of nitrogen remaining within the char. The C:N ratio then increases at 350°C which is indicative of loss of nitrogen compounds from the char at this temperature. Finally, the C:N ratio decreases again at 400°C which indicates that the remaining nitrogen stays within the char whilst a carbon-containing component is lost. This could again be explained by loss of methyl groups in the form of methane and is in agreement with the C:H data.

3.3 Degradation under 3% Oxygen in Nitrogen

3.3.1 Mass Loss Data and Observations

Following the degradation studies under nitrogen and air, a study was carried out under a 3% oxygen in nitrogen environment. A low oxygen environment is deemed to be more representative of a fire situation where depletion of the oxygen can occur quickly. The aim of this degradation study was, therefore, to determine if degradation of the foam in a low oxygen environment resembles the degradation under air or nitrogen, *i.e.* is thermal or thermo-oxidative degradation the dominant process in this situation. Presented in Figure 11 is a comparison of the quantities of residue obtained from the degradation of the foam under nitrogen, air and 3% oxygen in nitrogen. There is very little difference in the mass losses at 250°C under all three environments. As was the case during the degradation under air, the foam was discoloured following the degradation at 250°C under 3% oxygen in nitrogen. As the degradation temperature is increased it can be observed that the mass loss in 3% oxygen in nitrogen resembles the mass loss in air more closely than that under nitrogen, although the mass loss under the low oxygen environment is not as large. The mass loss data, therefore, suggests that thermo-oxidative degradation is more dominant when the foam is degraded in a low oxygen environment. Full analyses of the cold-ring fraction and char and tar components of the residues were undertaken as for the pyrolyses under nitrogen and air and

are reported in the supplementary material. These analyses, *in toto*, demonstrate that under the low oxygen environment thermo-oxidative degradation is more dominant, leading to charring of the foam at lower temperatures than under a non-oxidative environment. There are, however, differences observed between the degradation under air and 3% oxygen in nitrogen which indicates that the degradation is not simply oxidative in nature but also shows some non-oxidative characteristics.

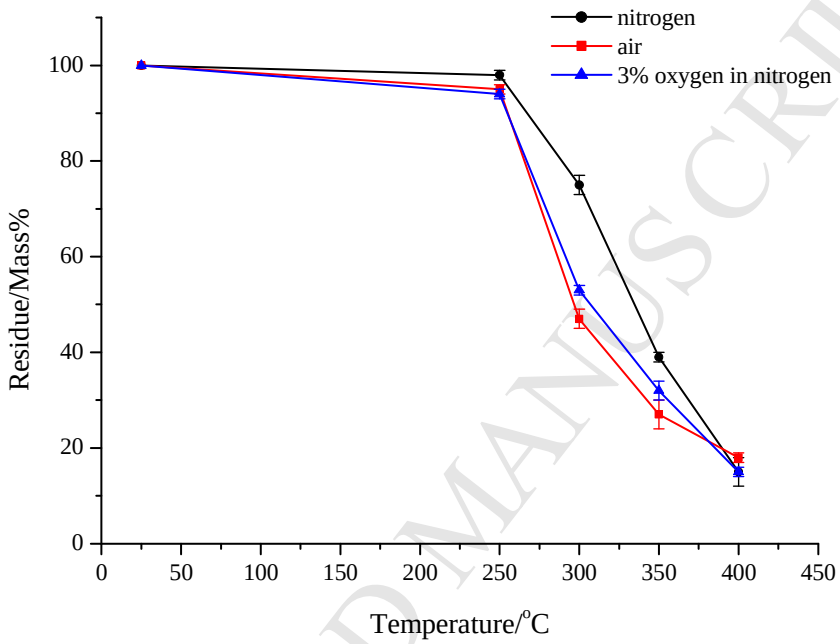


Figure 11: Residue obtained vs. degradation temperature for the foam under 3% oxygen in nitrogen

4. DISCUSSION

The results from the oxidative and non-oxidative degradation of the foam under nitrogen are interesting and provide an insight into the mechanisms of degradation of the polyurethane, in particular in the condensed-phase.

Results from the TVA studies [14] revealed that degradation of the urethane linkages under vacuum occurs by two competing mechanisms. The first mechanism, proposed to be the predominant mechanism, involves simple depolymerisation of the urethane bond to yield TDI and polyol. A second, competing, mechanism is proposed to occur which involves dissociation of the urethane linkages to yield diaminotoluene, carbon dioxide and alkene-terminated polyol chains. The degradation studies under nitrogen also reveal the presence of

these two competing degradation mechanisms for the urethane linkages, however, in this study diaminotoluene was observed as a major degradation product. Little degradation occurs upon degradation at 250°C, with no discolouration of the foam, and only a small mass loss. As the degradation temperature is increased the foam was observed to degrade more and the product profile indicates that this is a complex process. Both TDI and diaminotoluene were identified in the cold-ring fractions at 300°C and above which indicates that the urethane linkages are degrading by the two competing degradation mechanisms. Degradation of the urethane linkage by a depolymerisation reaction to yield TDI and polyol is proposed to occur initially; however, as the degradation is conducted under higher (atmospheric) pressure, more confined conditions, the diisocyanate cannot volatilise from the system as readily as under vacuum and so recombines with the polyol to reform the urethane bond. Under these conditions it is proposed that degradation of the urethane linkages *via* a six-membered ring transition state becomes the predominant reaction to form diaminotoluene, carbon dioxide and alkene terminated polyol chains. This proposal is supported both by the identification of C=C bonds in the FTIR spectrum of the tars at 300°C and above and by the presence of polyurea within the cold-ring fraction, which may suggest amines were formed.

Solid-state ^{13}C NMR spectroscopy of the chars indicates that at temperatures above 300°C ring fusion of the aromatic components within the foam occurs and this leads to a carbonaceous char which has a complex aromatic structure. In addition, elemental analysis results revealed that a significant quantity of nitrogen is present within the higher temperature chars, which confirms that the char is composed of nitrogen containing aromatic structures. It is proposed that under the confined conditions of the degradation the aromatic nitrogen-containing species, such as TDI and DAT, undergo secondary reactions and ring fusion to yield a complex char structure.

The results from degradation of the foam under air demonstrate that degradation of the polyurethane occurs at a lower temperature than under non-oxidative conditions and that the chemistry occurring in the condensed-phase is different.

After oxidative degradation at 250°C the foam was discoloured and a large quantity of tar was extracted which was shown to be highly polyol-based. Solid-state ^{13}C NMR and elemental analysis confirmed that a significant level of polyol had been lost from the char at this temperature. FTIR spectroscopy and GC-MS analysis of the cold-ring fraction at this

temperature revealed that the polyol had begun to undergo thermo-oxidative degradation to yield high molar mass polyol fragments, including cyclic species. The mass loss observed at this temperature, however, was small, indicating that chain scission to generate low molecular mass (and hence volatile) chain fragments was not extensive.

The solid-state ^{13}C NMR and FTIR spectroscopy results at 300°C revealed that almost complete loss of the polyol from the char had occurred by this temperature and few urethane linkages remained with the char. At this temperature the overall mass loss from the foam had reached almost 50% and it is proposed that significant thermo-oxidative degradation of the polyol had occurred by this temperature yielding volatile degradation products. The foam was also observed to be highly charred at this temperature and the solid-state ^{13}C NMR results revealed that the char consists of complex aromatic structures. The NMR spectrum at 400°C revealed that the methyl signal was almost completely lost by this temperature and, in combination with the elemental analysis results, it is proposed that at the higher temperatures under air the methyl groups are lost in the form of methane.

Analysis of the cold-ring fractions revealed a number of interesting points. The white polyurea residue observed during the degradation of the foam under nitrogen was absent during the degradation under air and this suggested that amines, in particular DAT, were not released during the degradation of this foam. The GC-MS analysis confirmed that DAT was not present in any of the cold-ring fractions. DAT arises from degradation of the urethane linkage *via* a six-membered ring mechanism which is proposed to be the predominant reaction under confined conditions when the TDI and polyol released from the depolymerisation reaction become trapped and recombine. The results, however, demonstrate that under an oxidative environment the polyol undergoes degradation at a much lower temperature than in an inert atmosphere. It is, therefore, proposed that the polyol does not reside within the degradation zone for as long and so cannot recombine with the TDI. Alternatively, the polyol may undergo oxidative degradation which prevents it from recombining with the TDI. The six-membered ring mechanism, therefore, would not occur to any great extent, which would explain the lack of polyurea residue during the degradation under air.

The GC-MS analysis, however, also revealed that TDI was absent from all of the cold-ring fractions. It may, therefore, also be the case that the TDI undergoes oxidative degradation

reactions which thereby prevent it from recombining with the polyol. The solid-state ^{13}C NMR results revealed that by 300°C the foam is highly charred and aromatic which indicates that aromatic components have already been incorporated into the char at this temperature. This, therefore, suggests that the TDI does undergo secondary reactions under air and explains the absence of this compound in the cold-ring fractions.

The results from the 3% oxygen in nitrogen degradation reveal that degradation of the foam in a low oxygen environment is complex, with both thermal and thermo-oxidative processes likely to occur. This is important and must be considered when developing new fire retardants systems for use within polyurethane foams, as any fire retardant must be able to work under both inert and oxidative conditions. These results also reinforce the issue that results from laboratory based degradation studies must be used with caution and may not necessarily be representative of a fire situation. In most cases degradation studies will deal simply with the degradation under air and/or nitrogen, not in a low oxygen environment.

5. CONCLUSIONS

Overall, the results presented in this paper and its predecessors have demonstrated that the thermal and thermo-oxidative degradation of a TDI-based polyurethane foam are complex processes which consist of different competing mechanisms which yield an array of volatile and involatile degradation products, as well as complex residues consisting of tar and char material. The results have also demonstrated that the degradation mechanisms of polyurethane are dependent on the experimental conditions of the degradation or degradation technique being employed.

Degradation studies under air revealed that degradation of the polyurethane occurs at a lower temperature than under non-oxidative conditions and that the chemistry occurring in the condensed-phase is different. The foam was observed to be highly charred by 300°C which confirms that the presence of oxygen alters or accelerates the charring reactions of the foam. During this degradation study neither TDI nor DAT were observed as major degradation products and there are a number of proposed reasons for this. The polyol is observed to undergo thermo-oxidative degradation at much lower temperatures than thermal degradation and so the polyol will not reside within the degradation zone for as long and so cannot recombine with the TDI. Alternatively the polyol may undergo oxidative degradation

reactions which prevent it from recombining with the TDI. In both these cases the six-membered ring transition state would not be dominant and as such DAT would not be evolved. The absence of TDI was proposed to be a result of this species undergoing oxidative degradation reactions which lead to it being incorporated into the char.

Finally, degradation in a low oxygen environment was shown to be a complex process, with the degradation behaviour lying between that of thermal and thermo-oxidative degradation. The foam begins to degrade and becomes more charred at lower temperatures than under nitrogen, however this is not as extreme as when the foam is degraded under air. It is, therefore, proposed that both thermal and thermo-oxidative degradation occurs when the foam is degraded in a low oxygen environment and this is important to understand when considering a fire situation and when developing new fire retardant systems. These results also reinforce the issue that results from laboratory based degradation studies must be used with caution and may not necessarily be representative of a fire situation. In most cases degradation studies will deal simply with the degradation under air and/or nitrogen, not in a low oxygen environment.

ACKNOWLEDGEMENTS

D.A. thanks the University of Strathclyde for the provision of a University Research Scholarship. We thank Dr David Apperley of the former EPSRC National Solid-state NMR Service at Durham University, UK, for the NMR data acquisition.

REFERENCES

[1] L. Shufen, J. Zhi, Y. Kaijun, Y. Shuqin and W. K. Chow, *J. Polymer-Plastics Technology and Engineering*, 2006, **45**, 95

[2] M. Ravey and E. M. Pearce, *J. Appl. Polym. Sci.*, 1997, **63**, 47

[3] N. Grassie and M. Zulfiqar, *J. Polym. Sci.: Polym. Chem. Ed.*, 1978, **16**, 1563

[4] Y. Zhang, Z. Xia, H. Huang and H. Chen, *Polym. Test.*, 2009, **28**, 264

[5] M. P. Thorne, *Can. J. Chem.*, 1967, **45**, 2537

[6] L. Låstbom, A. Colmsjö, R. Johansson, D. Karlsson, J. Melin, Y. Nordqvist, G. Skarping, Scandinavian Journal of Work, Environment and Health, 2003, 29, 152-158.

[7] N. Grassie, M. Zulfiqar and M. I. Guy, *J. Polym. Sci. Polym. Chem.*, 1980, **18**, 265

[8] D. Randall and S. Lee, *The Polyurethanes Book*, John Wiley and Sons Ltd, Everberg, 2002, Ch. 2, p. 9

[9] J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology: Part I. Chemistry*, Interscience Publishers, New York, 1962, Ch. II, p. 32

[10] N. Grassie and A. P. Mendoza, *Polym. Degrad. Stabil.*, 1984, **9**, 155

[11] G. G. Cameron, M. D. Ingram, M. Y. Qureshi, H. M. Gearing, L. Costa and G. Camino, *Eur. Polym. J.*, 1989, **25**, 779

[12] J. Fan and J. C. W. Chien, *Polym. Degrad. Stabil.*, 1985, **12**, 43

[13] L. Costa, G. Camino, M. P. Luda, G. G. Cameron and M. Y. Qureshi, *Polym. Degrad. Stabil.*, 1995, **48**, 325

[14] D. Allan, J.H. Daly and J.J. Liggat, *Polym. Degrad. Stabil.* , 2013, 98, 535-541

[15] N. Grassie and G. Scott, *Polymer Degradation and Stabilisation*, Cambridge University Press, Cambridge, 1985, Ch. 4, p. 86

[16] J. L. Boland and G. Gee, *Trans. Faraday Soc.*, 1949, **42**, 236

[17] G. Scott, *Atmospheric Oxidation and Antioxidants I*, Elsevier, Amsterdam, 1993, Ch. 2, p. 45

[18] D. K. Chattopadhyay and D. C. Webster, *Prog. Polym. Sci.*, 2009, **34**, 1068

[19] A.W. Benbow and C.F. Cullis, Combust. Flame., 1975, **24**, 217.

[20] R. Bilbao, J. F. Mastral, J. Ceamanos and M. E. Aldea, *J. Anal. Appl. Pyrol.*, 1996, **37**, 69

[21] Z. Wirpsza, *Polyurethanes: Chemistry, Technology and Applications*, Ellis Horwood, Chichester, 1993, Ch. 4, p. 121

[22] S. Khatua and Y. Hsieh, *J. Polym. Sci. Polym. Chem.*, 1997, **35**, 3263

[23] D. Wlodarczak, *J. Appl. Polym. Sci.*, 1988, **36**, 377

[24] H.H.G. Jellinek and S.R. Dunkle, *J. Polym. Sci.*, 1983, **21**, 487

[25] J. H. Daly, J. J. Liggat, L. McCulloch and R. A. Pethrick, Fire Retarded Flexible Foam, UK Patent Application PCT/WO2009/007715

[26] K. L. Erickson, *J. Therm. Anal. Calorim.*, 2007, **89**, 427 (2007)

[27] L. Costa, G. Camino, M. P. Luda, G. G. Cameron and M. Y. Qureshi, *Polym. Degrad. Stabil.*, 1996, **53**, 301

[28] T.C. Chang, W.S. Shen, Y.S. Chiu and S.Y. Ho, *Polym. Degrad. Stabil.*, 1995, **49**, 353

[29] T. Servay, R. Voelkel, H. Schmeidberger and S. Lehman, *Polymer*, 200, **41**, 5247